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THE PROBLEM OF THE FLASH OF EXPLOSIVES AND THE TRANSITION OF COMBUSTION INTO DETONATION

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/This article continues the discussion of long-standing disagreements between Belyayev and K. K. Andreyev on the subject of the upper flash limit and consists of several critical observations with reference to Andreyev's article entitled "The Flash of Explosives" (1). The reader is reminded that the point of view is Belyayev's throughout./

Two earlier works (2, 3) by Andreyev pointed out that no heat flash occurs under definite conditions for several explosives when the temperature is increased. Andreyev called this phenomenon the "upper thermal flash limit" and suggested that its cause was connected with chain or autocatalytic processes. However, the author later (4) showed that the "upper limit" phenomenon cannot be explained unless evaporation and the conditions under which the explosive's vapors form and move are taken into account. Belyayev also pointed out that the occurrence itself of the upper limit is associated with the phenomenon of vaporization. This latter statement is based on some experiments and on general postulates developed by the author (5, 6) with respect to the very important role the reaction in the gaseous phase, particularly the reaction in the vapor phase, plays in the combustion of explosives. No Soviet scientist disagrees with these assumptions. Moreover, it has been established that, even if the substance is nonvolatile or if evaporation cannot take place, combustion usually occurs in the gaseous phase. However, in this case, the gaseous phase is created by an auxiliary gasification reaction (7, 8).

The author showed (4) that the theory of thermal flash in the self-ignition of volatile explosives (most secondary explosives belong to this class) can be built up only on the basis that the flash occurs in the gaseous phase.

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Andreyev asserts (1) that the above explanation is erroneous and illogical, but immediately states that it is perfectly natural for an explosive to be converted into vapor if the temperature of the test tube is higher than the boiling point; that the conversion proceeds more rapidly as the temperature increases. However, this latter statement by Andreyev is the very heart of the explanation given by the author in his work (4), which was advanced prior to that of any other Russian scientist (Andreyev included) and which supplanted very unwieldy concepts. As a rule the flash lag cannot be accurately determined on the basis of the assumption that the temperature of the explosive is equal to the temperature of the furnace. Near the boiling point the temperature of the explosive should deviate from the temperature of the furnace. The amount of deviation should vary with temperature.

Working with small flash logs, Andreyev (2, 3) neglected to consider either the time necessary for heating the substance thoroughly or the temperature conditions in the test tube. He also failed to consider the possibility of evaporation and its effects.

In trying to disprove the author's point of view Andreyev modifies his earlier concept (2, 3) of upper limit by asserting (1) that: (a) if the temperature of the test tube is higher than the boiling point of the explosive, then the explosive can boil before flash occurs; (b) the self-ignition temperature of the vapors is greater than the self-ignition temperature of the condensed phase; and (c) when rapid evaporation occurs, the decomposition products are diluted appreciably by the vapors.

These statements are almost synonomous with the author's assumption which Andreyev previously termed "erroneous" and "illogical." Thus the difference in opinion concerns only the effect of evaporation.

The author asserted (4) that during violent evaporation the vapors leave the high-temperature zone so rapidly that there is insufficient time for them to be heated and for reaction to develop. Andreyev concludes (1) that the dilution of the decomposition products by the vapors is the essential factor, its importance heightened as the boiling becomes more violent. In this position Andreyev is probably close to the truth, since foreign research (9) has shown that the vapors of solid explosives have a somewhat greater flash lag than liquid-vapor systems. However, Andreyev's new position (1) reverses his former one (2, 3), and approximates the author's (4).

Such factors as the conditions of the thorough heating of the vapors, the conditions of their motion, and the possibility of their condensation in the cooler parts of the test tube do have an effect on the flash and cannot be ignored as done by Andreyev (1). Furthermore, Andreyev's contention that the vapors cannot move off to condense on cooler surfaces because they are heavier than air is incorrect. Andreyev himself (2, 3) noted this same phenomenon in a furnace with molten metal. The author's point of view and Andreyev's should both be considered to establish the true effect of evaporation. The factor of volatility which Andreyev considers "supplementary" to his explanation of the upper flash limit is actually the basis for the occurrence of this phenomenon. The selection of the term "upper flash limit" by Andreyev is unfortunate.

In connection with combustion stability and the transition of combustion into detonation, Andreyev repudiates the earlier assumption by the author (11) that the possibility of detonation resulting from flash is determined by the ratio of the boiling point to the temperature at which a vigorous reaction develops in the explosive.

It is true that later work by the author and other investigators have shown that the earlier assumption of the author cannot be taken as the basic and universal reason for the transition of combustion to detonation.

The chief reason for the transition of combustion into detonation is the disturbance of the equilibrium between the inflow and outflow of gas which takes place at a definite combustion velocity as first pointed out by the author (2). Andreyev is in error in his statement concerning the history of this problem (1) be declaring that he formulated this universally accepted concept simultaneously with and independently of the author. In 1946, Andreyev (14) did publish a paper in which he considered this problem, but his paper is a direct development and expansion of the author's idea published in 1940.

Andreyev's assertion that the author did not take into account (15) the fact that detonation occurs in the vapor phase for the case of boiling methyl nitrate is absolutely false. Andreyev probably did not have time to read the article carefully.

The results obtained in the work by Andreyev and Maslov (16), lead to the conclusion that, in general, detonation of gaseous mixtures do not readily cause the detonation of the explosive. Using detonating (hydrogen-oxygen) gas as the mixture, and nitrogelatin and TEN /Russian code name for an explosive/ as the explosives, the two authors showed (16) that detonation can be transferred at pressures below 15-20 atm. The authors experiments with methyl nitrate (15) showed that the detonation could be transferred from the vapor to the liquid at a pressure of 50 mm of mercury but that the detonation could not be transferred when boiling did not occur, even at the higher pressures. (The "favorable conditions" mentioned by Andreyev imply a state of violent boiling to the point where multitudinous bubbles are formed.) These are first heated thoroughly and then detonated, after which the detonation spreads to the whole liquid.

Recently, Andreyev suggested (17) a mechanism for the acceleration of combustion (leading to a limit for the rate of gas formation), which is based on Landau's "autoturbulence" theory (18). According to this theory, at some combustion velocity, a perturbation should occur in the liquid. The increase in the combustion velocity caused by this perturbation can, as shown by Andreyev, be rather large, exceeding the critical velocity. The author was the first (12) to show that there is a relation between the critical velocity and the disturbance of the gas balance.

Andreyev shows that the rate at which a disturbance should occur in a liquid should be about 0.25 g/sq cm sec for various explosives. It is true, for the substances he used, that when a combustion velocity is attained which causes turbulence there is an abrupt rise in the further increments of the combustion velocity and combustion becomes unstable. These statements are interesting, but "autoturbulence" does not explain the phenomenon entirely, since the nature of the instability of combustion is different in different cases. Turbulence caused by violent boiling or by intensive decomposition must be considered along with autoturbulence.

Even if the basic reason for instability is now clear, the factors which increase the combustion velocity up to the critical point are not yet completely understood, especially in the case of liquid explosives.

In conclusion, it should be noted that further investigation, particularly experimental investigations, is necessary to explain the mechanism of the transition of combustion to detonation in the case of liquid explosives.

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